Progress in the Development of RIMS for Quantifying Actinide Isotope Ratios for Nuclear Forensics Applications

B. H. Isselhardt, M. R. Savina, D. G. Willingham, K. B. Knight, I. D. Hutcheon

June 6, 2013

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Title: Progress in the Development of RIMS for Quantifying Actinide Isotope Ratios for Nuclear Forensics Applications

Authors: B.H. Isselhardt [1], M.R. Savina [2], D.G. Willingham [3], K.B. Knight [1], and I.D. Hutcheon [1]

Institutions: [1] Lawrence Livermore National Laboratory, Chemical Sciences Division
[2] Argonne National Laboratory, Materials Science Division
[3] Pacific Northwest National Laboratory, National Security Division

Abstract: We report progress in developing resonance ionization mass spectrometry (RIMS) for quantifying isotope ratios in U and Pu for nuclear forensic applications. We highlight recent improvements in instrumentation and methodology that have led to increased precision and stability in the measured isotope ratios. We also report measurements of U isotope abundance on several working reference materials and the corresponding uncertainty analysis. Finally, we will discuss outstanding issues for the routine application of RIMS to materials of nuclear forensics interest.

Introduction:

Resonance Ionization Mass Spectrometry (RIMS) can provide rapid isotopic data on actinide-containing materials without the need for time-consuming sample preparation and chemical separation procedures. Current techniques for determining U and Pu isotope compositions in solid samples for nuclear forensics, safeguards, and security applications face limitations with regard to analysis time, largely due to the requirements of sample preparation techniques required to remove isobaric interferences, which can take several days to complete. Through the use of element-specific laser ionization, RIMS is uniquely suited to the isotopic analyses of solid materials. RIMS uses lasers tuned to electronic resonances in an element of interest to achieve selective ionization of a single species. In brief, an expanding cloud of ions, molecules and neutral atoms containing all elements present in the sample is generated above the sample surface using a pulsed laser or ion beam. The secondary ions generated during this process are electrostatically rejected by applying a voltage pulse to the sample, leaving the neutral species behind. Neutral atoms of the element of interest are then selectively excited to an intermediate (resonant) electronic state by absorption of one or more laser photons tuned to characteristic transitions unique to the element of interest. This resonant excitation is made more selective through use of two or more resonant excitation steps (Figure 1). The excited atoms are then photoionized from the intermediate electronic state by an additional laser tuned to an autoionizing resonance (an unbound metastable state) above the ionization potential for the element of interest. Finally, these photoions are accelerated into a mass spectrometer, mass separated, and detected.

Early measurements of U isotope compositions in standards were aimed at determining present limits for reproducibility, and understanding the root causes of these limits. Our initial work to evaluate precision and accuracy of U isotope measurements by RIMS focused on measurements in U oxides (U_3O_8 and UO_2) [2,3]. Preliminary work in natural U-silicates [4] demonstrated precision measurement of U isotopes in minimally prepared samples. In this collection of initial work we concentrated on determining the resonance ionization laser parameters necessary to implement high-precision isotopic analysis of uranium.

The goal of the current effort is to demonstrate the quantification of $^{234}U/^{235}U$ and $^{235}U/^{238}U$ isotope ratios by Resonance Ionization Mass Spectrometry (RIMS) using materials from the NTNFC Uranium Methodology Project [5], to describe the methodology of RIMS measurements, define the current state-of-the-art capabilities, and identify needs for improvement. Recent instrument and method improvements have permitted reproducible measurements of the $^{235}U/^{238}U$ ratio to better than 0.3% relative standard deviation from the mean for over 10 hours. This allowed the study of previously unidentified sources of systematic bias of up to 2-5% between different samples in measurements performed using the CHARISMA instrument [6]. The observed bias is not inherent to the resonance ionization technique, but is due to CHARISMA's unique ion extraction hardware, originally designed for maximum sensitivity rather than maximum isotopic accuracy. We are currently modifying CHARISMA to achieve high accuracy.

Preparation of Standards and Samples:
Eight uranium samples were received at LLNL for analysis in support of the NTNFC Uranium Methodology Project [5]. The samples consisted of four U nitrate solutions and four U oxide samples. The samples were analyzed at LLNL for U isotopic composition, U elemental assay, and bulk chemical composition using a total of 9 analytical techniques. The samples were measured using each technique either four or eight separate times, in accordance with the project guidelines.

For the present work two of the solid materials were selected to serve as analytes: PTRM10-2.1 and PTRM1-2.2. Previous analyses by other methods at LLNL [5] indicate that PTRM10-2.1 is highly enriched U_3O_8 powder (~63% ^{235}U) and that PTRM10-2.2 is low-enriched UO_2 pellet (~4% ^{235}U). Aliquots of the two materials were collected from the previously processed aliquots of the LLNL samples, for PTRM10.2.1 this involved calcination of the powder at 900 °C for 2 hours, while the PTRM10.2.2 pellet was simply crushed for sub-sampling.

CRM U500 was used as a U isotope standard, it is a fine-grained U_3O_8 powder enriched to approximately 50% ^{235}U abundance, with certified abundances for ^{234}U, ^{235}U and ^{236}U relative to ^{238}U. As an initial test case, all three of these materials were prepared for analysis by pressing the samples into soft In foil secured on Al stubs compatible with the RIMS instrument. The two PTRM10 materials were mounted together on a single stub, and were pressed individually into the In foil with clean surfaces to minimize cross-contamination. The stub containing both PTRM10 materials is shown in Figure 2. The CRM U500 was mounted separately onto a stub in 5 different positions in order to help confirm the absence of position dependent bias in the measured uranium isotope ratios (position of the sample as held in the instrument for analysis), and is shown in Figure 2. Figure 3 contains pictures taken by scanning electron microscopy of the stub containing the PTRM10 materials (PTRM stub).

Modified Sample Preparation
Systematic effects in the measured isotope ratio were observed and will be discussed below. To test possible sources of these effects and eliminate sample topography or preparation effects a method was developed to optimize sample geometry and topography of the materials to be measured. Using the same type of aluminum stubs from the previous samples, 5 shallow craters were drilled directly in the Al face of the stub. Each of the three powdered samples was suspended in a drop of vacuum compatible epoxy and an aliquot of this slurry was placed into one of the shallow craters in the stub. The epoxy was cured overnight and then polished to give a flat smooth surface (1 micron finish) nearly level with the surface of the Al stub. One of these stubs is pictured in Figure 4, which contains PTRM10-2.1 in one spot, and U500 and PTRM10-2.2 in two spots each. Two duplicate stubs were prepared in this manner in order to test the reproducibility of measurements performed using CHARISMA on two different targets. The stubs were coated with ~8 nm of Ir metal to ensure conductivity across the samples in the epoxy.

Recent Instrument Improvements
Significant improvements to CHARISMA have been made in the past year, including the installation of a new ion detector. The higher gain and decreased "dead-time" of this detector enabled the reduction of analysis time by a factor of ten or, for the same analysis time, decrease the statistical uncertainty in isotope measurements by a factor of three. In addition, a grid system was implemented in the detector assembly that allows for increased rejection of background signals sometimes seen in "real world" samples. This modification has the potential to enhance CHARISMA's sensitivity for low abundance (parts-per-million and less) isotopes in the mass region of the actinides for a variety of matrices.

A system has been implemented to allow the resonance ionization lasers to "bounce back" or make a second pass through the ionization volume during the excitation and ionization step. This is advantageous for two reasons, first this provides for more efficient use of the laser energy allowing the saturation of the excitation and ionization processes over a larger volume, driving the processes well above saturation such that small variations in laser pulse energy have negligible effect on excitation probabilities. In addition, counter-propagating laser beams compensate for potential effects resulting from Doppler shifts of resonance wavelengths for sputtered atoms with significant velocity components parallel to the laser beams.

Counter-propagation requires that the laser beams be co-linear, meaning the laser beams are physically overlapped over a longer distance than in the original setup, where the laser beams traverse the ionization region at slightly different angles, and are only overlapped in the region of the ion extraction volume of the mass spectrometer. One aspect of co-linearity is that ions may be created in regions far from the center of the extraction volume, and may be biased in their relative isotope ratio.

Improvements also include the installation of new Q-switch systems in the lasers to better control and regulate the relative timing of the three pulsed laser beams. The Q-switches set the relative pulse timings of the lasers to within a nanosecond, and provide a means to prevent long-term drift of the relative laser timings.

Recent Measurement Results:

The recent improvements to CHARISMA, described above, allowed for an increase in ion current by a factor of ten while maintaining negligible dead-time effects and thus, acquire mass spectra 10x faster. This increased the precision of the measured $^{235}U/^{238}U$ ratio for several uranium oxide materials. The increase in count rate and decrease in measurement time decreased contributions to the standard uncertainty from statistical factors, revealing several sources of previously unidentified systematic bias, which are discussed below.

The $^{235}U/^{238}U$ isotope ratio was measured for CRM U500, on a single stub containing several populations of material distributed spatially across the stub (Figure 2, right). A single measurement of the $^{235}U/^{238}U$ ratio consisted of at least 40 records (each record containing information from 50,000 laser pulses). The mean of the individual records weighted by their standard uncertainty defines the measurement result. We measured the $^{235}U/^{238}U$ isotope ratio of U500 a total of 13 times across two days of experiments (>12 hours measurement time), which included a complete overnight shutdown of the laser system and instrument high voltage. Measurements were made at all five spatial positions on the U500 stub (Figure 2, right). All measurements of the $^{235}U/^{238}U$ isotope ratio are within 0.3% of the mean of the measurements. The results are shown in Figure 5, together with their weighted mean and a blue band representing ±0.3% of the mean. While all measurements from spot to spot on the stub are consistent within error, we did note that proper alignment of the sample surface with respect to the primary ion beam and the extraction optics by adjusting the height (or optical focus) of the stub was required. When the sample height was incorrect we observed bias in the measured isotope ratio on the order of 1-2%. The variation in sample height across this stub was a result of the mounting technique that relied on hand-pressing the powder into the In foil. Pressure was not applied uniformly, and the foil deformed to various degrees at different positions on the stub. This motivated the development of the modified sample preparation method utilizing polished surfaces.

The PTRM10 stub, with the analytes PTRM10-2.1 & 2, was installed on one of the three target positions within the instrument along with the U500 stub. Measurements of the $^{235}U/^{238}U$ ratio on both PTRM10-2.1 & 2 showed precisions of 0.3%, however there were systematic differences of up to 2% between these analytes and the U500 (relative to their known values). The bias in the measured $^{234}U/^{238}U$ ratios followed a similar pattern in systematic bias, although with larger uncertainties due to the low abundance of ^{234}U in the PTRM samples. Some of the observed systematic bias likely resulted from sample loading in two ways: 1) with the samples mounted by pressing powder into In, there can be differences when mounting the stubs into the sample holders inside the instrument, such that the top surface of the stubs and sample heights themselves are not necessarily loaded at the same height relative to the surface of the sample holders, and 2) there are possible variations in the high voltage at each target position that can result in different extraction fields, and therefore different biases in measured isotope ratios. This was confirmed by removing the PTRM10 stub from the instrument, re-adjusting the stub height, installing it back in the instrument on a different target position, rotated with respect to its previous orientation. The U500 stub was not moved in order to use it as a reference. The PTRM10 stub was measured again and significant changes, as large as 3%, in the measured $^{235}U/^{238}U$ and $^{234}U/^{238}U$ ratios relative to the previous measurements were observed. The measured isotope ratios on the U500 were consistent within error of the previous measurements, indicating that other sources of instrument bias stayed consistent.

The measurements described above demonstrated constant bias in the measurement result for U500 consistent within an estimated standard uncertainty of 0.3% across a period of 5 days, including restarting the instrument from a dead stop, *i.e.*, complete shutdown of the laser systems and venting of the mass spectrometer to atmosphere. Despite the high reproducibility of the measured isotope ratio in each material, however, significant systematic effects were observed in the accuracy of the measured isotope ratio relative to the "known" (certified) values. This motivated the mounting of U500 and the PTRM10 samples together at the same height on a single stub to minimize systematic effects from sample loading.

Analysis of Samples Prepared using the Modified Preparation Method
A modified sample preparation method was developed for eliminating possible systematic effects due to sample topography. Using two redundant sample mounts containing all desired analytes (PTRM10-2.1 & 2, and U500), isotope ratio measurements were obtained over several days. Each of the analytes displayed excellent reproducibility across several measurements during times of stable operating conditions, about 0.3% RSD from the measured means. However, systematic effects of about 1-2% in the measured $^{235}U/^{238}U$ ratio relative to the known value of the analytes were observed, despite the new sample preparation method. An example of this is shown in Figure 6, which contains the measured $^{235}U/^{238}U$ ratio relative to the known value for each of the three analytes for 4 measurements of each material over the course of a day (more than 10 hours real-time). The measured mean relative to the known value of each of these materials is shown as a dashed line in the corresponding color. In the absence of systematic effects, we expect that these three lines should overlap within the uncertainties of the measurements. Instead, the relative measured means of PTRM10-2.1 and 2.2 display differences of +0.95% and -1.6% relative to the measurement of U500, respectively. These differences are well outside of uncertainty due to statistical effects (~0.1%) and also much larger than the total estimated standard uncertainty of 0.3% (2σ). These systematic differences are not due to backgrounds, cannot be explained easily by cross contamination (HEU is more enriched and LEU is more depleted than expected), and are not constant with respect to sample position in the instrument.

Figure 7 presents the deviation of the individual measured isotope ratios shown in Figure 6 from the mean measured value of each corresponding analyte (black dashed line). This representation of the data relative to their respective measured mean highlights the reproducibility of measured isotope ratios and the stable operation of the laser system over a period of more than 10 hours, and neglects the systematic accuracy effects shown in Figure 6. The error bars are the estimated standard uncertainty of 0.3%. Here, systematic variance in measured isotope ratios cannot be explained by instability of the laser operating conditions, traditionally the dominant source of inaccuracy in RIMS measurements. These systematic effects must instead be due to the CHARISMA mass spectrometer system and its interaction with each sample as mounted, and not to instabilities in the laser ionization conditions.

The observed systematic effects were documented on multiple days and on duplicate sample mounts, but were neither constant nor consistent across the materials for different experimental sessions. The shifts observed in atomic isotope ratios were mirrored in the measured $^{235}UO_2/^{238}UO_2$ molecular isotopomer ratio, where the ions are produced by a non-resonant ionization process that is not affected by laser wavelength drift. In our experiments this ratio is monitored as an internal calibration reference for these pure uranium oxide materials (note that it would not a suitable

calibration tool in uncharacterized samples). The observation of systematic bias in the measured UO and UO_2 isotope ratios is consistent with the hypothesis that these effects are not due to the resonance ionization process in U atoms, but rather due to an instrument bias in ion extraction/transport in CHARISMA. Figure 8, for example, contains two charts showing the measured $^{235}U/^{238}U$ ratio relative to the known value for the three analytes as a function of time. The chart on the left shows the measured isotope ratio corrected for off-resonance background as would be performed for the analysis of an unknown, where the measurements are displayed as vertical lines representing the statistical uncertainty in determining the value of the measured isotope ratio for each record. A clear difference between the relative measured values of the three analytes can be seen, consistent with Figure 6, as well as a general trend in the measured value of U500 to increasing values of the $^{235}U/^{238}U$ ratio as a function of time. On the right side of Figure 8 the same measurements are shown, but each data point has been normalized by the $^{235}UO_2/^{238}UO_2$ ratio for that measurement and the known uranium isotope ratio. This correction is sufficient to make the measurements of each of the analytes consistent within statistical uncertainties, and can explain the observed systematic effects in the measured U isotope ratio between the different materials. There is still a clear upward trend in the measured isotope ratio, however, which is the result of changes in the laser system operating parameters during the measurement session. Note that in the absence of systematic bias induced by the mass spectrometer, bracketing the PTRM measurements by the U500 measurements would eliminate the drift trend due to changes in the laser parameters.

Discussion:
The ability to make the measurements described here has been enabled by the recent improvements to the stability of the laser system and the new detection system contributions to improved statistics, as well as the availability of these well-characterized reference materials. While the laser system can now provide stable measurement sessions across an entire day or even several days, this is not necessarily true for every experimental session. Work continues to understand the limitations and sources of laser system instabilities that affect measured isotope ratios. In the meantime, bracketing analyses can account for most of the measurement instabilities caused by the lasers.

The reproducibility of the measured isotope ratio across analytes, where the sequential analyses are interspersed across an entire day, eliminates laser system instability or drift as a source of the systematic effects. The measured isotope ratio of the UO_x molecules suggests that the systematic effects are significant for both resonantly ionized (U atoms) and non-resonantly ionized (UO and UO_2 molecules), and eliminates the resonance ionization process as a potential source of these systematic biases between materials. We therefore conclude that the source of systematic effects must be in the production/extraction/transport of ions produced by photoionization in CHARISMA, and is not inherent to the RIMS or resonance ionization process itself. Effort is underway to design experiments to investigate and quantify the sources of these systematic effects in measurements performed on CHARISMA.
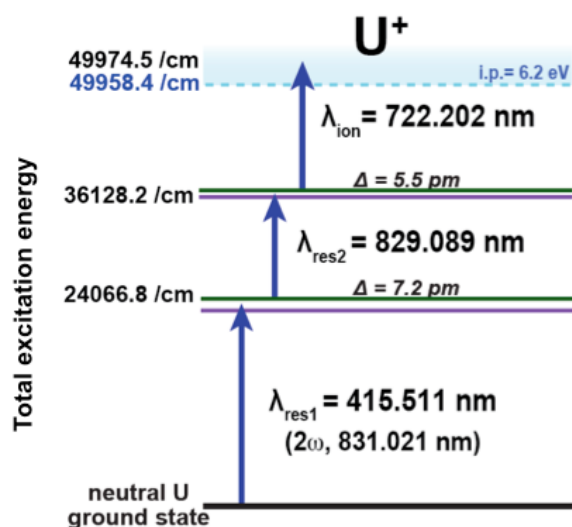
Figures:

Figure 1: *3-step resonant ionization scheme for U, adapted from Schumann, et al. [1] and modified to maximize uranium sensitivity and selectivity in our instrument. The green lines correspond to the resonance states of ^{235}U, the purple lines locate the ^{238}U resonances, Δ is the wavelength difference between the resonances of the two isotopes for a given transition.*
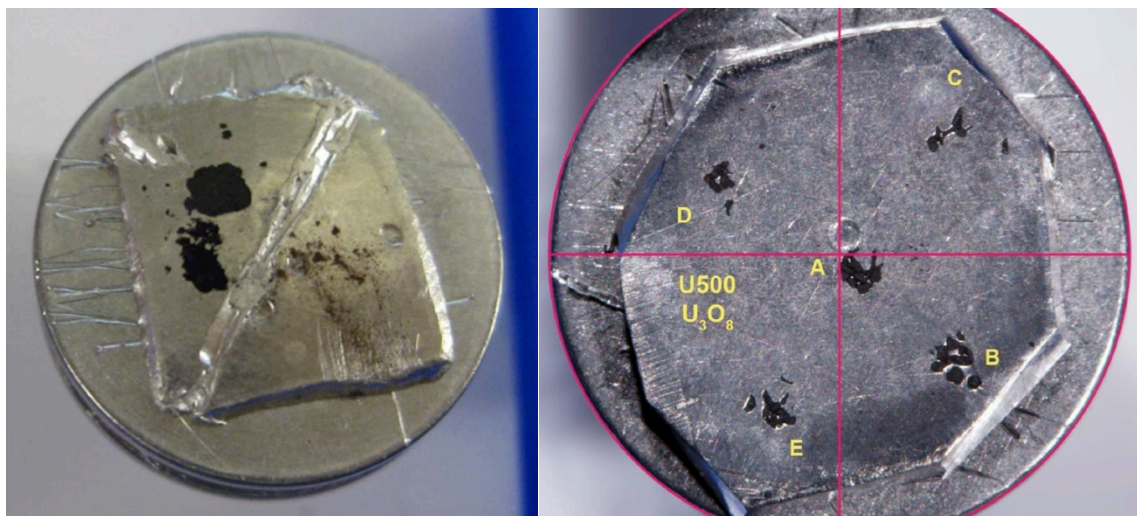

Figure 2: *Left: Optical image of PTRM10-2.1 & 2 pressed into In foil on an Al stub prepared for RIMS analysis. PTRM10-2.2 is to the left of the diagonal line and PTRM10-2.1 is to the right. The diameter of the Al stub is 12 mm. Right: CRM U500 powder pressed into In foil on an Al stub in 5 spatially distributed positions (A, B, C, D, and E). The diameter of the Al stub is 12 mm.*
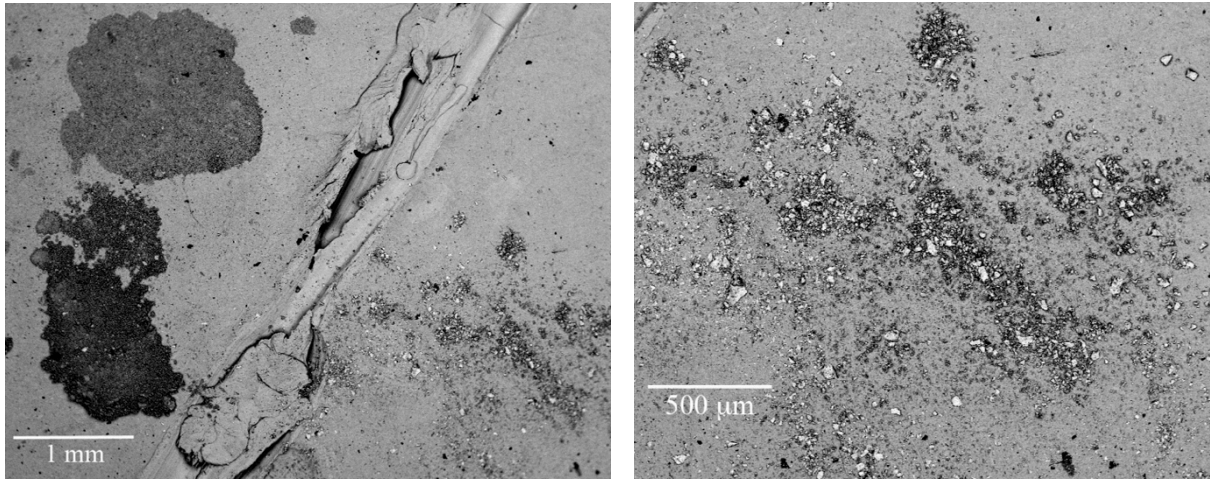
Figure 3: *Secondary electron images of PTRM10-2.2 (left) & 1 (right) pressed into In foil.*
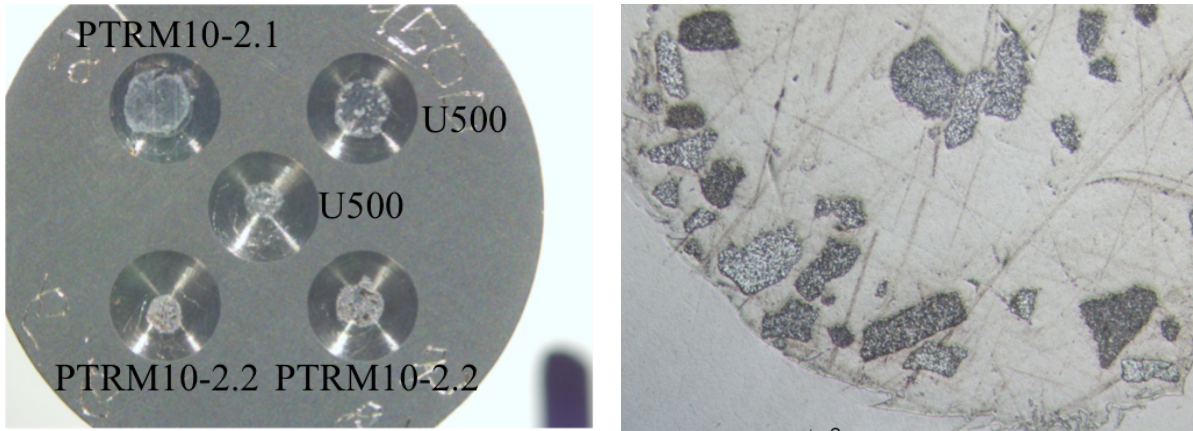

Figure 4: *Optical images of the modified sample mounting method, holding 5 samples in epoxy on an Al stub (left) and a 10X image (right) of the polished U500 grains in epoxy.*
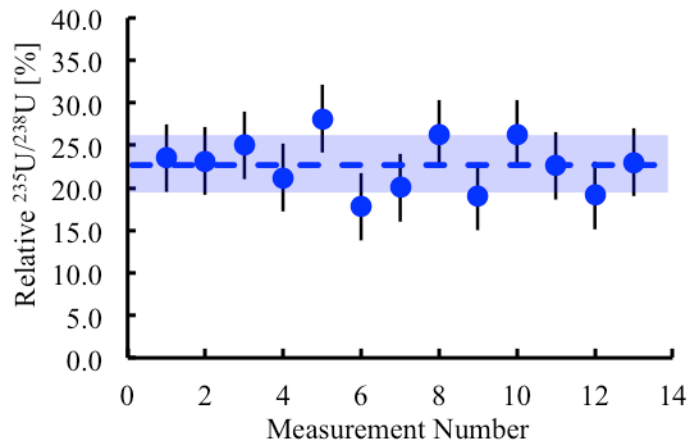

Figure 5: *Replicate measurements of the $^{235}U/^{238}U$ isotope ratio of U500 on two consecutive days, expressed as the difference between the certified value and the measured value in percent. The dashed line is the weighted mean and the blue band represents $\pm 0.3\%$ about the mean.*
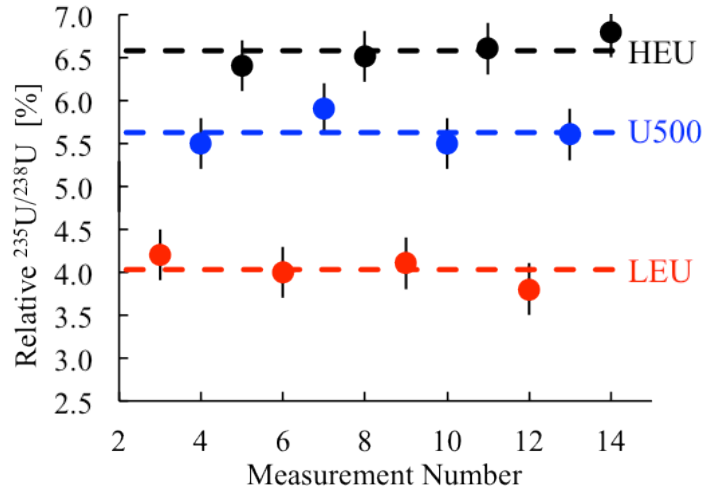
Figure 6: *Four replicate measurements of the $^{235}U/^{238}U$ isotope ratio of U500, PTRM10.2-1 & 2 over >10 hours, shown relative to their certified value. The dashed lines are the weighted mean of the measurements; the error bars represent the estimated standard uncertainties of 0.3% (2σ).*
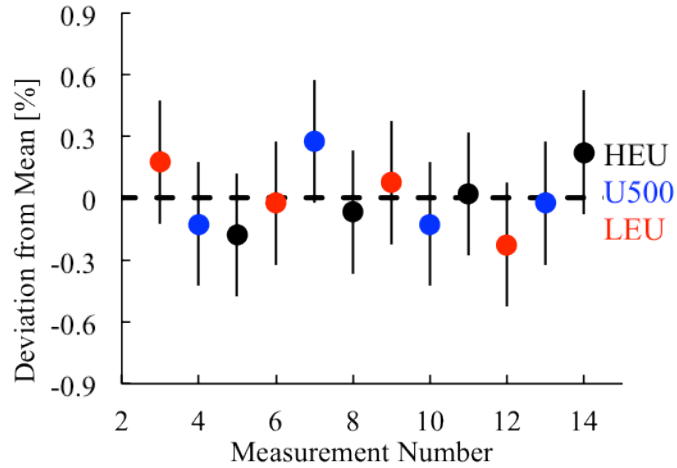

Figure 7: *Deviation of the measured $^{235}U/^{238}U$ isotope ratio relative to the measured mean of each of the analytes. The measurements were obtained over a period of 10 hours. Error bars are estimated standard uncertainties of 0.3%.*
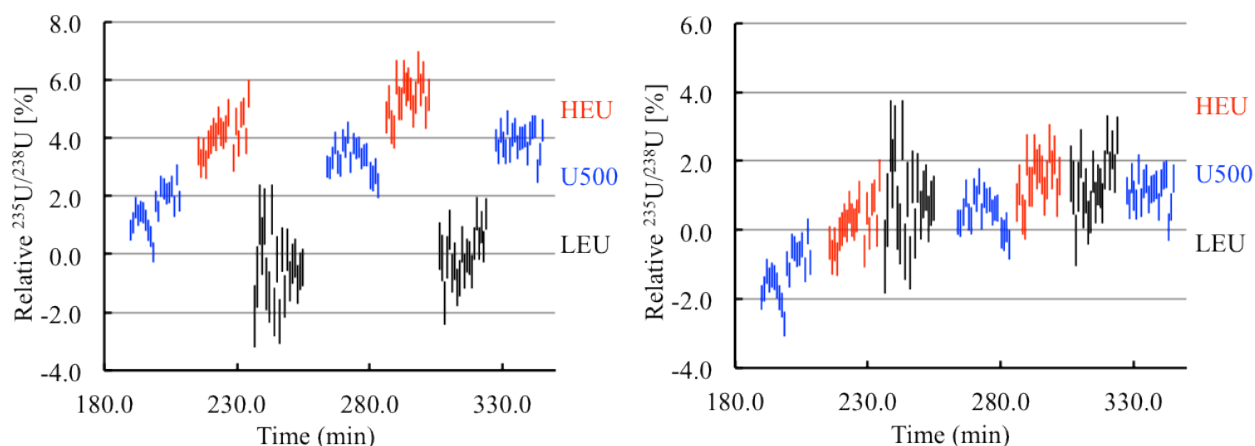
Figure 8. *Left: The measured $^{235}U/^{238}U$ ratio as a function of time for the three analytes expressed as Δ, the percent deviation from "known" value. Each line represents an individual record of the measured isotope ratio (integrated over 50,000 laser shots); the length of the line is the 2σ uncertainty from statistical sources. Right: The same measurements normalized by the $^{235}UO_2/^{238}UO_2$ ratio (m/z 267/270) for the each record. The remaining upward trend in the data represent a drift in the $^{235}U/^{238}U$ ratio caused by slight drifts in laser wavelength and timing.*

References:

[1] Schumann, P.G.; Wendt, K.D.A. & Bushaw, B.A., High-resolution triple-resonance autoionization of uranium isotopes, *Spectrochim. Acta, Part B*, 2005, 60, 1402-1411.

[2] Isselhardt, B. H.; Savina, M. R.; Knight, K. B.; Pellin, M. J.; Hutcheon, I. D. & Prussin, S. G., Improving Precision in Resonance Ionization Mass Spectrometry: Influence of Laser Bandwidth in Uranium Isotope Ratio Measurements, *Anal. Chem.*, 2011, 83, 2469-2475.

[3] Knight, K. B.; Savina, M. R.; Isselhardt, B. H.; Prussin, S. G.; Pellin, M. J. & Hutcheon, I. D., Rapid uranium isotope measurements of solids by Resonance Ionization Mass Spectrometry, *in press, 2012*.

[5] Knight, K.; Savina, M.; Isselhardt, B.; Hutcheon, I.; Prussin, S. & Pellin, M., Uranium Resonance Ionization Mass Spectrometry in Natural U-silicate, *Proceedings in Radiochemistry,* 2011, 1, 37-43.

[5] Uranium Methodology Performance Testing: Analytical Results for Uranium Isotopic and Chemical Composition of Bulk Uranium Materials, LLNL, 2010, LLNL-MI-453631.

[6] Savina, M. R.; Pellin, M. J.; Tripa, C. E.; Veryovkin, I. V.; Calaway, W. F.; Davis, A. M., Measuring presolar grains with CHARISMA, *Geochim. Cosmochim. Acta* 2003, 67, 3215-3225.